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STARK SHIFTS OF THE VISIBLE ABSORPTION SYSTEMS OF THE NO_2^- ION IN $NaNO_2$

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Stark effect measurements on the lowest triplet and singlet transitions of the nitrite ion show that the change of dipole moment on excitation is very small (ca. 0.30 D) and of opposite sign for the two states. The dipole moment change in the triplet manifold is also found to distinctly depend on vibrational (ν_2) excitation. This is explained as a result of vibronic coupling among B_1 triplet states.

1. Introduction

Since Hochstrasser and Noe have reported the Stark splitting of absorption lines of azulene in a naphthalene host crystal [1], much work has been done to extract molecular properties from observed Stark phenomena in spectra of molecular crystals.

A serious problem in the analysis of the data however, is the general existing lack in knowledge of the local field on the molecular site. Therefore, comparison of molecular parameters with the results of theoretical calculations is ambiguous.

One way to more or less evade this problem is to collect *relative* Stark data of various spectral bands of the same molecule, rather than attempting to obtain *absolute* values. The local field indeed is not expected to change rapidly on vibronic excitation and to a good approximation can therefore considered to be constant.

The present work deals with the determination of Stark shifts of some triplet and singlet absorption bands of the NO_2^- ion in a $NaNO_2$ single crystal.

Low temperature triplet and singlet absorption spectra of this system were previously reported by Hochstrasser and Marchetti [2] and Sidman [3] and the spatial symmetry of the absorbing states was determined to be B_1. The main feature of these spectra is the existence of long progressions in the bending vibration ν_2, which indicates that considerable changes in geometry occur on excitation of this ion [2]. The presence of these progressions makes the NO_2^- ion a very suitable candidate for a study of the change in dipole moment on vibrational excitation.

Stark shifts of several members of the ν_2 progression in the $^3B_1 \leftarrow {}^1A_1$ absorption system are reported in this paper. The observed shifts are found to be rather small. Only through the use of a multichannel detection system [4], we were able to measure these shifts with sufficient accuracy to detect significant changes in dipole moment on vibrational excitation in the $^3B_1$ state.

Unfortunately, as the $^1B_1 \leftarrow {}^1A_1$ absorption is extremely intense, for this absorption system only a shift of the electronic origin of some traps in the crystal could be measured.

The measured dipole moment changes are found to be in good agreement with the outcome of ab-initio calculations performed by Jonkman [5] on the vertical transitions. The vibrational dependence of the dipole moment in the triplet manifold is further explained as the result of vibronic coupling among B_1 triplet states.

A simplified model for "borrowing" dipole moment analogue to the HT theory for "borrowing" transition dipole moment between two coupling states was recently presented by Clark and Small [6] and is used here to analyse our results.

2. Experimental

Large single crystals of $NaNO_2$ were prepared using

the Bridgeman technique. The starting material was reagent grade $NaNO_2$ (Merck), which was used without further purification. The crystals are orthorhombic (space group Im n2 [7,8]) whereby the molecular x (out of plane), y, and z (C_2 axis) axes are parallel to the crystal a, b and c directions, respectively. The orientation of the crystals was determined by locating the cleavage (± 110) planes. For the Stark experiments, the crystals, sawn along the ab plane, were polished and placed between stainless steel electrodes. The thickness of the crystals used was about 1 mm. All measurements were carried out at about 1.5 K and square wave high voltage modulation up to 9 kV, at a 1 Hz repetition rate, was applied over the crystals.

The optical set-up consisted of a 1000 W xenon lamp as the light source, a Spex "Minimate" which was used as a predisperser, and a Spex 1704 spectrometer, provided with an echelle grating (300 grooves/mm, Bausch and Lomb).

The detection system was a multichannel analyzing system, which is described elsewhere [4]. In contrast to conventional one channel scanning systems the spectrometer in this set-up is held at a fixed wavelength position. The spectrum is dispersed on a vidicon, and the resulting video signal is decoded into a real spectrum and accumulated.

The vidicon used in our set-up was an RCA 4532 A silicon diode array type and the spectra were accumulated and stored in a computer of average transients (CAT, Varian C-1024 with some modifications). After a prefixed measurement time the spectra stored in the memory of the CAT were read out digitally in the form of an array of 512 numbers, which were fed in a digital computer to perform the required calculations.

3. Analysis of the results

For a proper understanding of the way followed to analyse the results we will briefly explain here the applied modulation technique. Fig. 1 shows two different waveforms frequently used to the high voltage modulation in our experiments, resulting respectively in an M_1 and an M_2 modulation spectrum. Also the add/subtract command signal for the CAT, wherein the accumulation of the modulation spectrum takes place, is shown in the picture.

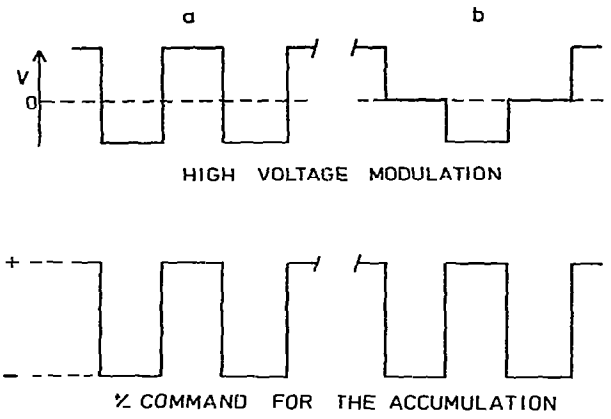

Fig. 1. Waveforms used for the high voltage modulation and of the add/subtract command for the accumulation, to obtain an M_1 (a) or an M_2 spectrum (b).

If there exists an inversion center in the crystal system studied, the M_1 spectrum will cancel, because the Stark effect is then invariant to a sign change of the applied electric field. In the $NaNO_2$ crystal, however, there is no inversion symmetry: all NO_2^- dipoles are oriented along the same crystal c axis. Indeed, only when the electric field is applied along the c axis, do we observe an M_1 spectrum. An example of such a modulation spectrum is given in fig. 2.

We also apply high voltage modulation during the accumulation of the *absorption* spectra. Therefore, as a function of the detector current $I(\lambda, E)$, at wavelength λ and applied electric field E, the absorption spectrum $A(\lambda, E)$ and the modulation spectrum $M_1(\lambda, E)$ can be expressed as:

$$A(\lambda, E) = \tfrac{1}{2}[I(\lambda, +E) + I(\lambda, -E)] ,$$

$$M_1(\lambda, E) = I(\lambda, +E) - I(\lambda, -E) .$$

As the shift $S(E)$ can be determined as the half of the difference between the first moments of absorption spectra with positive and negative electric field, $S(E)$ can be expressed as:

$$S(E) = \frac{1}{2}\int_{-\infty}^{\infty} \ln\left[\frac{A(x,E) + \tfrac{1}{2}M_1(x,E)}{A(x,E) - \tfrac{1}{2}M_1(x,E)}\right] x\,\mathrm{d}x \times \left\{\int_{-\infty}^{\infty} \ln\left[\frac{A(x,E) + \tfrac{1}{2}M_1(x,E)}{I_0}\right]\mathrm{d}x\right\}^{-1} , \qquad (1)$$

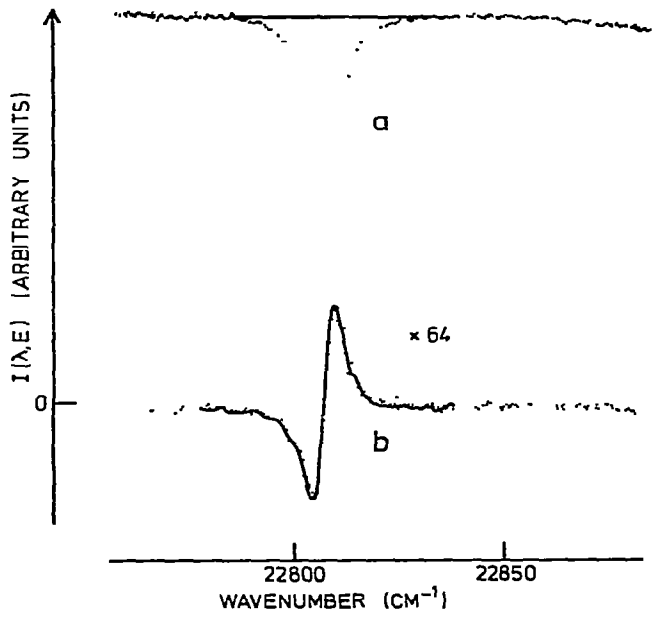

Fig. 2. The 6 × ν_2 overtone of the $^3B_1 \leftarrow {}^1A_1$ absorption system (a) and the corresponding Stark modulation spectrum (b). The electric field (34.6 kV/cm) was applied along the c direction of the crystal. The dots in the picture are the experimental values and correspond to the constants of the channels of the CAT. The solid line in the modulation spectrum represents the simulated modulation spectrum, by subtracting two absorption spectra, shifted by the calculated amount.

where I_0 is the detector current outside the absorption. The transformation to optical density units, used in (1), is to eliminate the effect of electric field induced line broadening.

In (1) we suppose that no intensity change in the absorption takes place when an electric field is applied. This was checked by simulation of the modulation spectrum by subtracting two absorption spectra, shifted by the calculated amount. Such a simulated spectrum is also shown in fig. 2. In all cases good agreement was found between the simulated and the actual modulation spectrum.

4. Stark shifts

A Stark effect was *only* observed when the electric field was applied along the c axis of the crystal, being the direction of the NO_2^- C_2 axis. This Stark effect appeared to be a pure shift linearly depending on the applied electric field. The ratio of the shifts of various absorption bands of the same crystal, measured under the same circumstances, was found to be very constant. However, a comparison of Stark shifts of *different* crystals showed much more deviation in outcome. This is probably caused by field inhomogeneity and a slight misalignment of the crystals. Therefore, while the reported *ratios* are obtained using all measurements (42) at all crystals (7), the scaling factor was obtained by averaging values resulting from the four best reproducing crystals.

4.1. The $^3B_1 \leftarrow {}^1A_1$ absorption system

The origin of this absorption system is located at 18959 cm^{-1}. The spectrum is dominated by an extensive progression in the ν_2 vibration, with a characteristic frequency of 644 cm^{-1}. We measured the Stark shift of the origin and of the first six members of the ν_2 progression.

The values obtained are listed in table 1.

4.2. The $^1B_1 \leftarrow {}^1A_1$ absorption system

As expected for a spin and orbitally allowed transition, the singlet absorption is extremely intense, even in very thin crystals. Therefore, no Stark data could be obtained using pure crystal singlet absorption bands. However, as shown in fig. 3, some other, medium intense, origins are present in the spectrum, belonging

Table 1

Absorption	Stark shift × 10^3 in cm^{-1} at 1 kV/cm	$\Delta\mu$ (exp) [a] (debye)	$\Delta\mu$ (calc) [b] (debye)
$^3B_1 \leftarrow {}^1A_1$			
0 × ν_2	−6.4 ± 0.4	−0.28 ± 0.02	
1 × ν_2	−5.8	−0.24	
2 × ν_2	−5.2	−0.23	
3 × ν_2	−4.8	−0.21	−0.20
4 × ν_2	−4.7	−0.20	
5 × ν_2	−4.2	−0.18	
6 × ν_2	−4.5	−0.19	
$^1B_1 \leftarrow {}^1A_1$			
0 × ν_2	+7.2 ± 0.4	+0.31 ± 0.02	+0.3

a) An anisotropic Lorentz approximation is used, with F_L = 1.38.

b) From ab initio calculations of Jonkman [5], for vertical transitions.

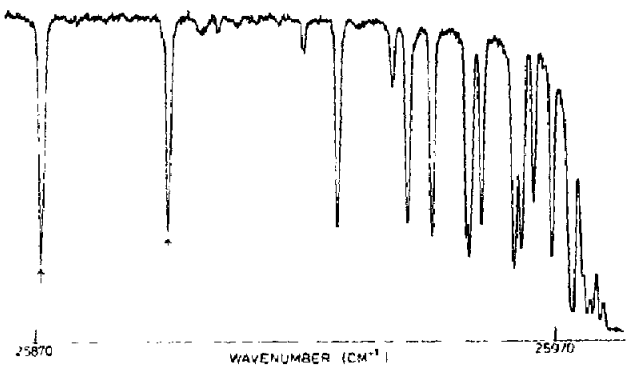

Fig 3. The region of the origin of the $^1B_1 \leftarrow {}^1A_1$ absorption spectrum The sharp, medium intense, lines are due to several traps in the crystal At two of these lines, the indicated ones in the picture, the Stark shift was measured.

to several traps in the crystal. Stark shifts were determined for two of such trap origins, located respectively at 25871 and at 25896 cm^{-1}, yielding the same shift within the limit of the experimental error. A roughly corresponding value was obtained by measuring the Stark shift of the pure crystal fluorescence origin Although in the latter case the modulation spectra were too noisy to enable accurate measurements, these two facts are a strong indication that the Stark shift of the trap origins is also characteristic of the pure crystal electronic origin. The Stark shift is given in table 1.

Finally, an anisotropic Lorentz approximation, taking the local field $F_L = (N^2 + 2)/3 = 1.38$, was used to calculate the differences in dipole moment of the ground state and the absorbing states. These values are also listed in table 1, together with results of theoretical ab-initio calculations [5].

5 Discussion

It is rather surprising, in view of the large change in geometry on excitation, that the absolute changes in dipole moment are rather small compared with the dipole moment of the ground state. Also the sign inversion of the dipole moment change going from the ground state to the $^3B_1$ and the $^1B_1$ states is noteworthy and indicates that on excitation rather subtle changes must occur in the charge distribution over the ion

Because our experimental results are in good agreement with $\Delta\mu$ values calculated by Jonkman [5] for vertical transitions, we choose the same absolute signs for the $\Delta\mu$'s as the calculated ones.

Furthermore, table 1 shows a significant decrease in the observed Stark shifts going from the electronic origin to higher numbers of excited ν_2 quanta of the triplet state.

The conventionally used model for calculating the change in dipole moment on electronic excitation is in fact a crude adiabatic Born–Oppenheimer approximation, being independent of vibrational excitation. The imperfection of this approximation for the *transition* dipole is well known, as it is inadequate to explain phenomena as "false" origins in spectra. The usual way to account for these effects is to expand the transition dipole about a symmetric equilibrium configuration, which causes mixing of the Born–Oppenheimer states (Herzberg–Teller effect). Analogue to this "borrowing" of transition dipole between coupling BO states there is also a "borrowing" of permanent dipole moment between these states. As was recently pointed out by Clark and Small [6], this will result in a dipole moment which depends on the number of excited vibrational quanta in an electronic state.

Returning to the case of the NO_2^- ion, the HT coupling must occur with a $^3B_1$ state, since the promoting ν_2 mode is of a_1 symmetry According to McEwan [9] there is another $^3B_1$ state situated 5.56 eV above the lowest triplet state. Following ref. [6], taking into account only coupling among the lowest $^3B_1$ states, we write

$$\Delta\mu(g) = \Delta\mu^{CA} + (2g + 1)\,\mu_{\nu_2}\,, \qquad (2)$$

where $\Delta\mu^{CA}$ is the difference between the crude adiabatic dipole moments of the ground state and the excited state, and g is the number of excited ν_2 quanta. In the harmonic approximation, μ_{ν_2} is given by ‡:

$$\mu_{\nu_2} = (\alpha^2_{JF,\nu_2}/\Delta^2_{JF})(\mu^{CA}_J - \mu^{CA}_F) + (M_{JF}/\Delta_{JF})(\alpha_{JJ,\nu_2}\alpha_{JF,\nu_2}/\Delta_{JF} - \beta_{JF,\nu_2})\,, \qquad (3)$$

where F and J are the absorbing and coupling state, respectively, $\alpha_{JF,\nu_2} = (\hbar/2\omega_{\nu_2})^{1/2}\langle J|\partial H/\partial Q|F\rangle$, with

‡ This expression has previously been obtained by Clark and Small [6], eq. (11), except for an arithmetic error which has been corrected.

ω_{ν_2} the angular frequency of ν_2, $\beta_{JF,\nu_2} = (\hbar/2\omega_{\nu_2})\langle J|\partial^2 H/\partial Q^2|F\rangle$, Δ_{JF} is the difference in energy between the states J and F, and M_{JF} is the transition dipole between these states.

Fitting the experimental data of table 1 to a straight line, which can be done within the limits of the experimental errors, and comparing the regression constants with (2) we obtain:

$$\Delta\mu^{CA} = -0.275 \pm 0.004 \text{ D}, \quad \mu_{\nu_2} = +0.008 \pm 0.001 \text{ D}.$$

Using eq. (3) to obtain a theoretical value for μ_{ν_2}, a detailed knowledge is required of the geometry and the wavefunctions of the coupling $^3B_1$ state. Unfortunately, such data are not available yet. Since in (3) terms of about equal magnitude interfere, it also seems not simple to make an estimate of the size of μ_{ν_2}.

However the above analysis shows that the simple H–T coupling theory at least explains the physics behind our observations.

6. Conclusions

The observed Stark effect on the triplet and singlet absorption spectra of the NO_2^- ion in $NaNO_2$ is only due to a change in dipole moment. The observed dipole moment changes on excitation, which are of opposite sign for the triplet and the singlet state, compare very well with theoretical calculations.

It further turns out that the dipole moment is dependent on the number of ν_2 vibrational quanta in the NO_2^- ion, which is consistent with a HT model for "borrowing" dipole moment.

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